



Short communication

Pt nanoparticles ion-implanted onto indium tin oxide electrodes and their electrocatalytic activity towards methanol

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H I G H L I G H T S

- ▶ A versatile and green strategy for the fabrication of PtNPs onto ITO using an ion-implanted method.
- ▶ Small size PtNPs exhibits well catalytic performance and stability towards the electrooxidation of methanol.
- ▶ PtNP/ITO electrode may be a more suitable electrode material for the direct methanol fuel cell.

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A versatile and green method is developed to ion-implant novel Pt nanoparticles (PtNPs) with an energy of 21 keV at a fluence of 1.0×10^{17} ions cm^{-2} onto indium tin oxide (ITO) electrodes. The morphology and structure of the PtNPs are characterised by scanning electron microscopy (SEM), revealing that the diameters range from 2 to 12 nm and the average radius is 8 nm. Based on the electrochemical oxidation of methanol, we find that the PtNP/ITO electrode exhibits excellent electrocatalytic activity, which could be useful in fuel cells.

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1. Introduction

Fuel cells are a very promising energy source due to their low pollutant emission and high energy-conversion efficiency. The development of an efficient catalyst for direct methanol fuel cell (DMFCs) is a key step in achieving high efficiency. Platinum is widely considered to be the best single-metal catalyst for methanol oxidation; however, the poisoning of platinum catalysts by intermediates, such as CO_{ads} , is a serious problem [1–3].

Many approaches have been used to synthesise Pt nanoparticles (PtNPs), including the chemical reduction of Pt precursors by reducing agents, electrochemical deposition and surfactant- or ligand-based colloidal methods. However, these methods are complicated and time-consuming and some steps require elevated temperatures [4–6].

Ion implantation is a versatile and green technique for forming nanocrystalline precipitates embedded in the near-surface region of a wide variety of crystalline and amorphous host materials.

This method can modify the structure of a target near surface by bombardment with metal ions [7,8]. Our group had recently reported the PtNP-modification of indium tin oxide (ITO) electrodes using ion implantation for the electrochemical detection of nitrite and hydrogen peroxide [9]. The electrode exhibited a very low background current and excellent electrochemical stability, even after ultrasonic treatment, indicating the high stability of the metals at the ITO surface. In addition, very few articles apply the ion-implantation method to fabricating PtNP-modified ITO electrodes, and even fewer address its applications in DMFCs.

In the present paper, we report for the first time a simple method for adding PtNP onto low-cost ITO substrates by ion implantation. The PtNP/ITO electrodes were used for the electrocatalytic oxidation of methanol and exhibited remarkable catalytic activity and high stability.

2. Experimental

2.1. Electrode modification

ITO glass was obtained from the Beijing Tsinghua Engineering Research Center of Liquid Crystal Technology. A sheet of ITO glass

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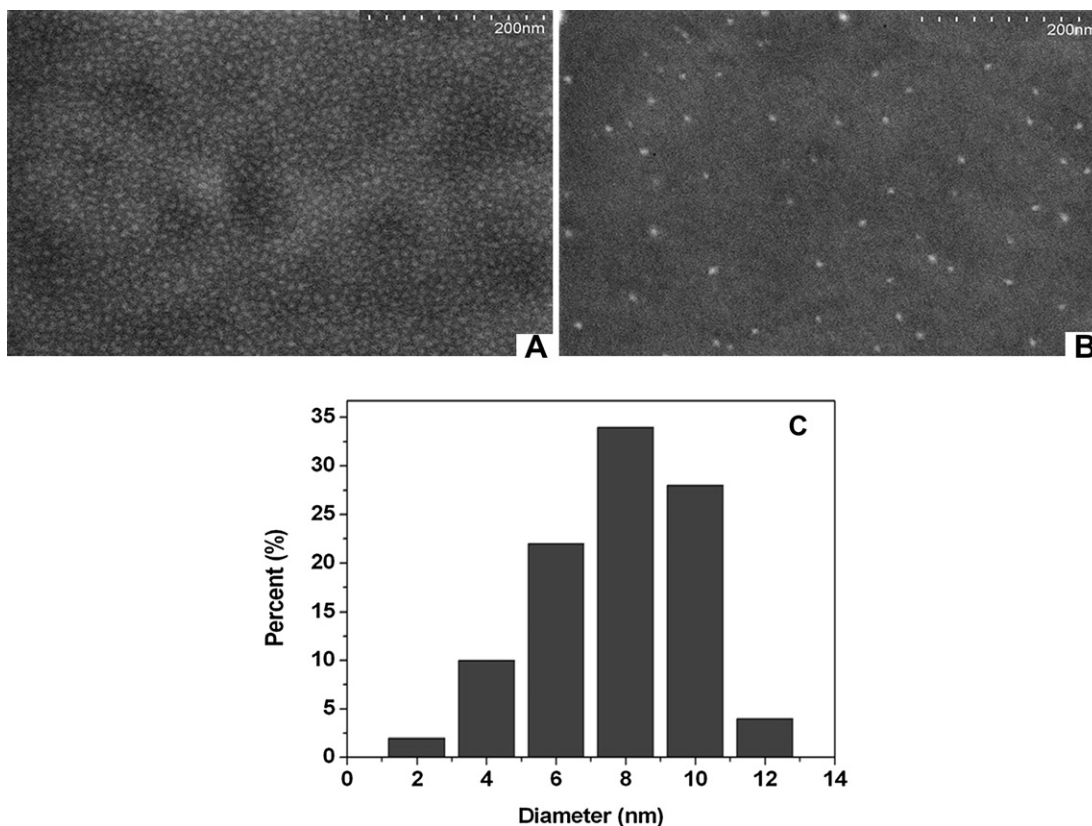


Fig. 1. SEM images of the bare ITO electrode (A) and the PtNP/ITO electrode (B) and the diameter distributions of the PtNP/ITO electrode (C).

was cleaned ultrasonically in triply distilled water, ethanol and then again with triply distilled water for 5 min. Ion implantation was performed using a Beijing Normal University (BNU) metal vapour vacuum arc (MEVVA) implanter at room temperature. Additional details about the preparation and the MEVVA implanter are provided elsewhere [9,10]. Of the Pt ions, 14% were simply charged, 75% doubly charged and 11% triply charged, and then these Pt ions with 21 keV at a fluence of 1.0×10^{17} ions cm^{-2} were implanted onto the ITO surface, forming the PtNP/ITO thin film.

2.2. Characterisation

SEM images were obtained using an X650 SEM (Hitachi, Japan). Electrochemical measurements of the PtNP/ITO electrodes were

performed on a CHI660D electrochemical workstation (CH Instruments, China). The electrochemical measurements were carried out using a three-electrode system: a bare or ion-implanted ITO electrode with an exposed geometric area of 0.5 cm^2 as the working electrode, Ag/AgCl (saturated KCl) as the reference electrode and a Pt wire as the counter electrode.

3. Results and discussion

Fig. 1 shows a typical set of SEM micrographs and diameter distribution histograms for PtNPs ion-implanted onto ITO electrodes. The quasi-spherical PtNPs have been successfully immobilised onto the ITO electrode with diameters between 2 and 12 nm, averaging 8 nm.

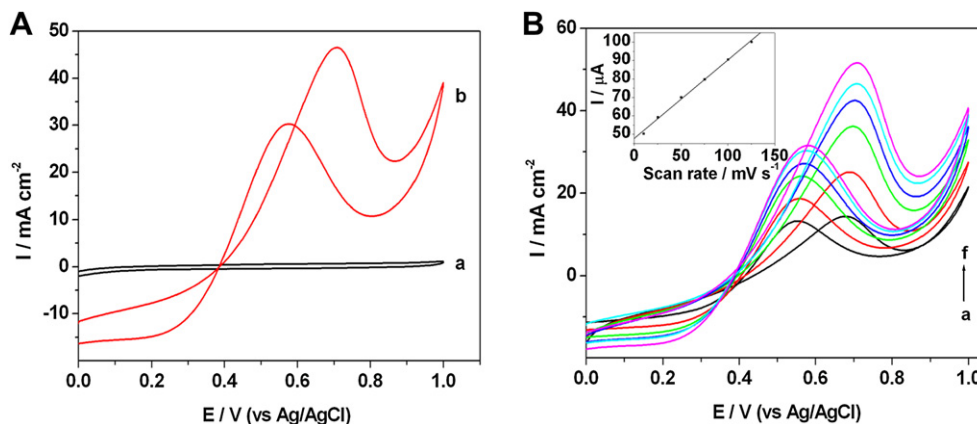


Fig. 2. (A) CV in N_2 -saturated $1.0 \text{ M CH}_3\text{OH} + 0.1 \text{ M H}_2\text{SO}_4$ for the bare ITO electrode (a) and the PtNP/ITO electrode (b), scan rate: 100 mV s^{-1} . (B) CV in N_2 -saturated $1.0 \text{ M CH}_3\text{OH} + 0.1 \text{ M H}_2\text{SO}_4$ for the PtNP/ITO electrode. Inset: peak currents versus scan rates.

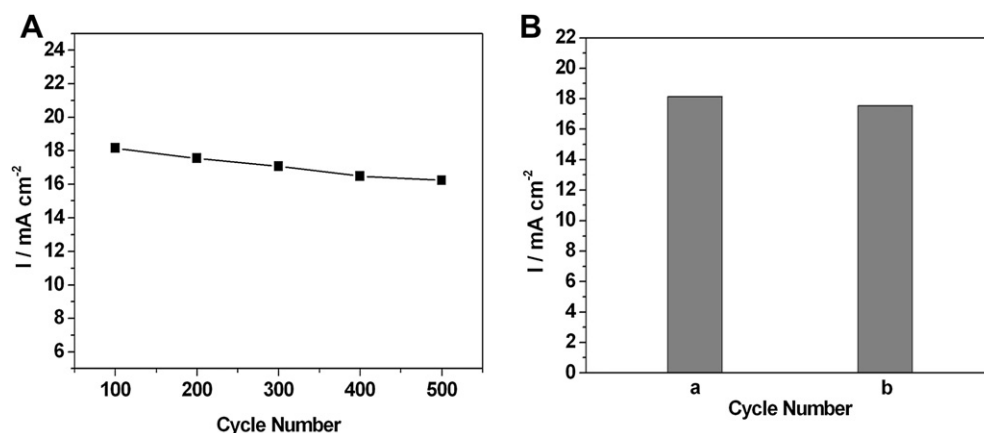
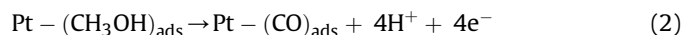
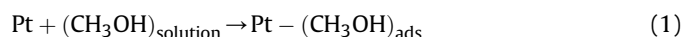


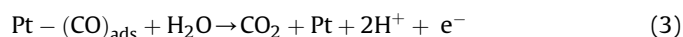
Fig. 3. (A) The relationship between the forward peak current density and the cycle number at 100 mV s^{-1} in $1.0 \text{ M CH}_3\text{OH} + 0.1 \text{ M H}_2\text{SO}_4$. (B) The recovery ability of the PtNP/ITO electrode after 500 continuous cycles: column a, the first cycle; column b, the 501st cycle in freshly prepared solution.

Fig. 2A shows the electrochemical properties of PtNPs in terms of methanol oxidation by cyclic voltammetry (CV) at a PtNP/ITO electrode in $1.0 \text{ M CH}_3\text{OH}$ containing $0.1 \text{ M H}_2\text{SO}_4$. The background current of the bare ITO electrode (curve a) is very small, with no redox peaks for methanol oxidation, indicating that bare ITO has no electrocatalytic activity for methanol oxidation. A typical response to the electrocatalytic oxidation of methanol is observed at PtNP/ITO electrode. Two irreversible current peaks (curve b) are observed during the methanol oxidation: a forward scan peak at 0.71 V and a backward peak at 0.57 V , attributed to the adsorption and interaction of various intermediate species at the surface of the active sites of Pt [11]. The PtNP/ITO electrode showed a greater negative shift of the oxidation potential than materials described in earlier studies: 100 mV lower than that of Pt-coated gold nanoporous films (0.85 V) [12] and 245 mV lower than that of Pt/C-coated glassy carbon electrodes (0.995 V) [13]. Although the oxidation potential was the same as that of Pt/SWCNT [14], the peak current was enhanced significantly, suggesting high electrocatalytic activity for methanol oxidation.

The oxidation peak at 0.57 V indicated that methanol was easily adsorbed on the PtNP-modified electrodes and that the alcohol dehydrogenation reaction followed the adsorption behaviour described in reactions (1) and (2) [15,16]:



The peak current at 0.71 V was attributed to the reoxidation of strongly adsorbed CO species produced by the alcohol dehydrogenation, which occur as follows:



During the above process, the formation and adsorption of intermediates (CO and CO_2) poisoned the electrode surface [17]. We could apply the ratio of the forward peak current density (I_f) to the reverse peak current density (I_b) to determine the tolerance of PtNPs to the poisonous intermediates. This ratio was higher for the PtNPs on the electrode (1.57) than for PtNP/CNT (1.00) [18]. The results reflected that the PtNP/ITO electrode possessed a high resistance to CO or other specimens during methanol oxidation and that the PtNP/ITO electrode had a good electrocatalytic activity towards the electrooxidation of methanol. The PtNP/ITO electrode is more CO-tolerant than PtNP/CNT because of the role of ITO in the interaction. ITO has a weaker interaction with CO than carbon-

based substrates, such as CNT or carbon black, because CO cannot be avoided completely.

Fig. 2B shows the CVs of methanol electro-oxidation at the PtNP/ITO electrode in $1.0 \text{ M CH}_3\text{OH}$ containing $0.1 \text{ M H}_2\text{SO}_4$ at different scan rates. The results demonstrate that the forward peak current is a linear function of the scan rate (inset of Fig. 2B), indicating that methanol electro-oxidation is an adsorption-controlled process. The linear regression equation is $i_{\text{pa}} (\mu\text{A}) = 4.7756 + 42.5909 \nu$ (mV s^{-1}), with a correlation coefficient of $r = 0.9985$.

Fig. 3A shows that the peak current density of methanol oxidation obtained from the forward CV sweep decreases gradually with cycle number. At the 500th cycle, the peak current density is 89.4% (16.22 mA cm^{-2}) of that (18.15 mA cm^{-2}) at the first cycle. Fig. 3B shows the results of a control experiment: after 500 cycles, the catalyst was again investigated by CV in freshly prepared $1.0 \text{ M CH}_3\text{OH} + 0.1 \text{ M H}_2\text{SO}_4$ aqueous solution, exhibiting a peak current density of 17.55 mA cm^{-2} , which was 96.7% of that at the first cycle. This finding suggests that the main cause of the decrease in the current density in the continuous 500 cycles may be the consumption of methanol. The excellent long-term cycle stability of the PtNPs further implies that ion-implanted PtNPs may be a good alternative catalyst for use in DMFCs.

4. Conclusions

In this work, PtNPs have been fabricated onto ITO electrodes by ion implantation to prepare a novel functional electrode. SEM results indicate that the PtNPs were immobilised on the ITO electrode surface with the average size of 8 nm . The small size of the PtNPs may greatly improve the electrochemical performance of the PtNP/ITO electrode, which exhibits good catalytic performance and stability towards the electrooxidation of methanol. This PtNP/ITO electrode may be a more suitable electrode material for DMFC.

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